INFLUENCE OF SOME INTERCALATIONS ON ACTIVATION OF PRE-BAKED CLAY

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ABSTRACT

We report on the influence of temperature, mixing ratio and holding time of NaOH & KOH intercalations on the surface area, micropore volume and micropore width of pre-baked clay samples. Pore size & surface area analyzer was used to measure the surface area, micropore volume and average pore width using Dubinin–Radushkevich (DR) method. A meaning full effect was observed when the temperature was increased from ambient up to 150 °C in case of both intercalating agents. Increasing temperature beyond 150 °C caused a decline in surface area generation even up to 750 °C. The results also show that mixing ratio has a positive effect on the porosity and the micropore surface area increases as the mixing ratio increases in case of both intercalating agents. The influence of holding time shows two different trends. In case of NaOH, the porosity increases as the time increases while in case of KOH, the porosity decreases as the time increases. SEM, EDX and XRD studies were also performed. The results show effective insertion of the sodium and potassium into the clay matrix thereby causing generation of porosity.

Keywords: clay; baked clay; activation; intercalation; dubinin–radushkevich (DR) method

INTRODUCTION

There is a tremendous interest in research on nanostructure materials in recent years due to their superior sportive, chemical, thermal and mechanical properties¹⁻⁶. Nanostructure materials are enjoying popularity in catalyst preparations. Moreover, they are considered as effective adsorbents for pollutants removal /sequestration. As, it is well established that surface topography and internal interface structure of the materials is known to substantially affect their bulk properties⁷. Therefore, there is a need to look in to these properties.

There are various approaches by which such materials can be activated. Some investigators have used different chemicals to open up the blind pores and to increase emptiness in the internal structure⁸. Acid leaching procedure for the porous materials activation is reported in the literature⁹. Some adsorbents are activated using zinc chloride as intercalation agent¹⁰. Phosphoric acid also shows good activation ability¹¹. In addition, some researchers have reported methods other than chemical activation. Physical activation with steam to get high micropore¹² and irradiating with gamma rays have been documented in the literature¹³. Activating clay using simultaneous chemical as well as physical activation is extensively reported¹⁴⁻¹⁶.

We report on the use of NaOH and KOH as intercalating agents to pre baked clay, separately. The influence of temperature, mixing ratio and holding time on porosity, micropore volume and pore width is discussed.

EXPERIMENTAL

Collection of sample

Pre-baked clay sample was collected from a local brick kiln according to the standard method of sample collection, ground, and dried in an oven at 105 °C in order to remove the surface moisture. The clay understudy was analyzed by electron dispersive energy scattering (EDS) technique. The EDS signature along with the composition is provided in Fig. 1.

Fig. 1. EDS signature of original clay.

Solvent intercalation

Aqueous solutions of NaOH and KOH (AR grade) were prepared in desired percentages i, e 1 %, 5 % and 10 %. Baked clay samples were intercalated in

a vat with NaOH and KOH, separately while varying the temperature, mixing ratio of intercalating agents and holding time of intercalation.

Effect of temperature

For evaluating the temperature influence on surface area, micropore volume and micropore width, one g portions of baked clay sample were subjected separately to solvent intercalation using aqueous solutions of NaOH, KOH. 10 ml aliquot of the respective solution was added to each sample and heated at 150 °C, 500 °C and 750 °C, respectively. Each of the hydro thermally treated samples was washed with copious amount of de-ionized water, dried in a vacuum oven at 70 °C in order to remove all the surface and entrapped moisture. The prepared samples were kept in vials for determination of surface area, micropore volume and micropore width.

Effect of mixing ratio

In order to study the effect of mixing ratio on surface area, micropore volume and micropore width of the clay understudy, one g of sample was subjected to solvent intercalation using NaOH, KOH prepared in concentration of 1 %, 5 % and 10 %, separately. Further, treatment was done in a similar fashion as described above.

Effect of holding time

For studying the time influence, one g of baked clay sample was subjected to same intercalations performed for time duration of 5hr, 15hr and 24hr, separately. Each of the hydro thermally treated samples was washed exhaustively with deionized water till free of alkali, dried in a vacuum oven and analyzed as under.

Surface area, micropore width and micropore volume analysis

For the determination of surface area and pore volume, the whole and variously intercalated samples were analyzed using pore size and surface area analyzer Model (Quanta Chrome Nova 2200e) under the conditions reported elsewhere⁸. The surface area and micropore volume were calculated using Dubinin–Radushkevich Method (DR method) (drmethod)¹⁷. Average pore width was calculated using the formulae: $\frac{2V}{A}$

Where

V is volume and A is the area of the pores

SEM Analysis

SEM micrographs of the original and variously intercalated clay samples were obtained by Scanning Electron Microscope (SEM) Model JSM 5910 JEOL Company Japan. Each of the samples was mounted on a disc and coated with gold.

EDX Analysis

Energy dispersive X-ray spectrophotometer (EDX) Model Inea 200, Made UK, company oxford was used for the analysis of original clay sample.

XRD Analysis

X-ray diffraction (XRD) analysis of the samples was done with X-ray diffractometer (Rigaku Tokyo) using Cu K α radiation generated at 35 kV, 20 mA. Each sample was filled in an aluminum sample holder and scanned in a step-scan mode [0.05(o)/step] over the angular range of 8°–30° (2 θ).

RESULTS AND DISCUSSION

Clay under study was analyzed by EDS. The chemical composition is provided in Fig.1 which shows that the clay under trial is enriched in oxides of silicon and aluminum with calcium, potassium and titanium as minor constituents. In addition, the matrix contains iron oxide as next abundant mineral. The presence of sulfur evidents the existence of sulphides and sulphates of Si, Al, Ca, K, and Ti in small quantities. From the data it is affirm that the clay under study mainly belong to smectite group of clay with general formula of $C_{0.5}(Si_4Al_8Fe_2)(Fe_{3.5}Al_4Mg_1)O_{20}(OH)_4$.

The influence of parameters like temperature, mixing ratio and holding time of intercalation using NaOH and KOH on the porosity, pore volume and pore width of pre-baked clay has been evaluated

Effect of temperature

Activation of baked clay was performed at 150 °C, 500 °C, and 750 °C. The changes in surface area, micro pore volume and pore width as a function of temperature is provided in Table 1.

Table 1. Changes in surface area, pore width, & micropore volume as a function of intercalation temperature.

Temperature (°C)	Surface area (m ² /g)		Pore width (Å)		Micropore volume (cc/g)	
	NaOH	KOH	NaOH	KOH	NaOH	KOH
Original	96.00	96.00	6.250	6.250	0.03	0.03
Ambient	71.90	58.87	8.344	6.794	0.03	0.02
150	140.48	201.68	7.110	6.941	0.05	0.07
500	112.68	183.56	7.099	7.626	0.04	0.07
750	73.92	52.87	8.116	7.565	0.03	0.02

The surface area determined in case of NaOH & KOH treatments at ambient temperature was 71.90 m² g⁻¹ and 58.87 m² g⁻¹, respectively. In the next set of experiments, the temperature was increased upto 150 °C. The surface area determined in case of NaOH was 140.48 m² g⁻¹ and in case of KOH was 201.68 m² g⁻¹. The temperature was further increased to 500 °C. The surface area determined in case of NaOH was 112.68 m² g⁻¹ and in case of KOH was 183.86. In the next step; the temperature was further increased to 750 °C. The surface area determined in case of NaOH was 73.92 m² g⁻¹ and in case of KOH was 140.48 m² g⁻¹.

From the data compiled in Tables 1, it can be seen that surface area is increased significantly when the temperature is increased from ambient to 150 °C. The effect is more pronounced in case of KOH where a manifold increase in surface area is observed. The reason can be thought is heating to this level, the removal of sorbed water molecules is expedited and the significant moisture out gassing opens up the otherwise blind pores causing alterations in pores dimensions. The increase in surface area in case of both metal hydroxides also corresponds to their tunneling effect under soft hydrothermal conditions¹⁸.

The significant increase in case of potassium intercalation compared to sodium is due to the size of the inserting ion which in turn caused effective tunneling in the matrix compared to sodium which is of small size and instead of tunneling, some other structures might have generated due to poor advective and diffusive action of sodium. It is well established that the size of tunnels corresponds to the size of the templates inserted¹⁹.

It can be observed from the data assembled in Table 1 that a decline in surface area is resulted when the sample was heated up to 500 °C followed by heating up to 750 °C. This adverse effect on surface area when the temperature was increased from 150 °C - 750 °C is attributed due the fact that increase in temperature causing the onset of decomposition of the discrete mineral inclusions in the matrix leading to formation of respective metal oxides thereby causing a decline in the surface area of the matrix²⁰. It is also observed that both metal hydroxides caused a decrease in the surface area and this decrease

in both cases is quite significant particularly at high temperature (750 °C). The reason can be thought is the super plastic behavior of alkali metals to form eutectics at high temperature with the already present inorganic elements in the matrix or to coagulate other elements to form clusters²¹ leading to clogging of pore channels.

The nitrogen adsorption isotherms of the aforementioned original and variously intercalated samples are provided in Figs 2 (a) & 2 (b). The DR plot of the representative sample is provided in Fig. 3. All the isotherms obtained reveal hysteresis loop with a definite plateau. The major nitrogen adsorption occurs at low relative pressures indicating that the clay is porous with narrow pore size distribution. Upon comparing the isotherms obtained in case of sodium and potassium intercalations at ambient temperature, followed by 150 °C, followed by 500 °C, followed by 750 °C, it seems simple that porosity of the clay under study was increased significantly when it was heated at 150 °C with either of the intercalating agents.

Fig. 2 (a). Nitrogen adsorption-desorption isotherms of original clay and clay intercalated with NaOH as a function of temperature: 1= virgin, 2= room temperature, 3 = 150 °C, 4 = 500 °C, 5 = 750 °C.

Fig. 2 (b). Nitrogen adsorption-desorption isotherms of original clay and clay intercalated with KOH as a function of temperature: 1= virgin, 2= room temperature, 3 = 150 °C, 4 = 500 °C, 5 = 750 °C.

Fig. 3. Dubinin–Radushkevich plot for original clay sample.

In order to ascertain the influence of temperature on the pore width, the clay was treated separately with NaOH and KOH at ambient temperature, 150, 500 and 750 °C. The pore width determined in case of NaOH at ambient temperature was 8.344 Å and in case of KOH was 6.794 Å. The temperature was then increased to 150 °C. The pore width determined in case of NaOH was 7.110 Å and in case of KOH was 6.941 Å. The temperature was further increased up to 500 °C. The pore width determined in case of NaOH was 7.099 Å and in case of KOH was 7.626 Å. The temperature was next increased to 750 °C and the pore width determined in case of NaOH was 8.116 Å and in case of KOH was 7.565 Å.

It can be seen a marginal change in average pore width when the clay was heated progressively in the presence of the aforementioned intercalating agents. This can be ascribed to the formation of tunnels and eutectics & topotectics microstructures or directional solidification, hence leaving behind a solid with wider pores. The effect of temperature on pore widening of elutriite has already been reported in the literature ²².

Experiments were performed in a similar fashion in order to evaluate the influence of temperature on the pore volume. The micropore volume determined at ambient temperature for NaOH treated clay was 0.03 cc/g and for KOH was 0.02 cc/g. The temperature was then increased to 150 °C. The value obtained in case of NaOH was 0.05 cc/g and in case of KOH was 0.07 cc/g. The temperature was next increased to 500 °C, the pore volume determined in case of NaOH was 0.04 cc/g and in case of KOH was 0.07 cc/g. The temperature was further increased to 750 °C. The values of pore volume were; for NaOH, 0.03 cc/g and for KOH, 0.02 cc/g. The reasons visualized for this increase in pore volume are similar as given in the case of porosity.

Effect of mixing ratio

Activation of baked clay was performed with 1 %, 5 % and 10 % mixing ratios. The changes in surface area, pore volume and pore width as a function of mixing ratio are provided in Table 2. The surface area determined at zero concentration was 53.78 m² g⁻¹. The intercalating agents were then applied to the clay in 1 %, 5 % and 10 % mixing ratio. The surface area determined in case of 1 % NaOH was 53.12 m² g⁻¹, and in case of KOH was 51.90 m² g⁻¹. The ratio was then increased to 5 %. The surface area determined was; for NaOH, 103.84 m² g⁻¹ and for KOH, 114.34 m² g⁻¹. The mixing ratio was further increased to 10 % and the values obtained were; for NaOH, 140.48 m² g⁻¹ and for KOH, 201.68 m² g⁻¹. The data shows that increase in mixing ratio has a positive effect on surface area generation in case of the clay under study.

It is affirmed from the data provided in the Table 2 that surface area shows a linear increase with the increase in concentration of the metal hydroxide. This is attributed due to the fact that when we increase the concentration, the particles swell or dilatate due to the imbibition of NaOH and KOH which in turn exert pressure on the walls of the pore leading to widening and lengthening in pore dimensions. As afore mentioned, the increase in surface area corresponds mostly to tunneling ability of the metal ions under study. Thus, increase in ion concentration leads to a more tunnel formation thereby resulting an increase in surface area ²³.

Table 2. Changes in surface area, pore width, & micropore volume as a function of intercalation ratio.

Intercalation ratio (%)	Surface area (m ² /g)		Pore width (Å°)		Micropore volume (cc/g)	
	NaOH	KOH	NaOH	KOH	NaOH	KOH
0.0	53.78	53.78	7.437	7.437	0.02	0.02
1.0	53.12	51.90	7.530	7.707	0.02	0.02
5.0	103.84	114.34	7.704	6.996	0.04	0.04
10.0	140.48	201.68	7.118	6.941	0.05	0.07

The nitrogen adsorption isotherms of the aforementioned variously intercalated samples are provided in Figs. 4 (a) & 4 (b). The major nitrogen adsorption occurs at low relative pressures indicating that the material is porous with narrow pore size distribution. Upon comparing the isotherms obtained in case of sodium and potassium hydroxide at 0 %, 1 %, 5 % and 10 %, it is evident that porosity of the clay under study was increased significantly with the increase in concentration of both intercalating agents.

Fig. 4 (a). Nitrogen adsorption desorption isotherms of original clay and clay intercalated with NaOH as a function of concentration: 1= virgin, 2=zero concentration, 3= 1%, 4= 5%, 5= 10%.

Fig.4 (b). Nitrogen adsorption desorption isotherms of original clay and clay intercalated with KOH as a function of concentration: 1= virgin, 2=zero concentration, 3= 1%, 4= 5%, 5= 10%.

In the next step of experiments, the effect of mixing ratio on the pore width was evaluated. The increase in concentration was kept at the same frequency as above.

The average pore width determined at zero mixing ratio was 7.437 Å. In case of 1 % NaOH, pore width determined was 7.530 Å, while in case of 1 % KOH, it was 7.707 Å. The mixing ratio was next increased up to 5 %. The value obtained in case of 5 % NaOH was 7.704 Å, and in case of KOH was 6.996 Å. The values obtained in case of 10 % NaOH and KOH were 7.118 Å and 6.941 Å, respectively.

The micropore volume values determined at zero mixing ratio were; in case NaOH, 0.02 cc/g, and in case of KOH, 0.02 cc/g. Similarly, in case of 1 % NaOH, micropore volume determined was 0.02 cc/g, while in case of 1 % KOH, it was 0.02 cc/g. In case of 5 % mixing ratio, the value obtained for NaOH was 0.04 cc/g, and for KOH was 0.04 cc/g. For 10 % NaOH and KOH, the micropore volumes determined were 0.05 cc/g and 0.07 cc/g, respectively.

The overall effect of metal hydroxide concentration on the pore properties can be ascribed to the efficient etching resulting in more pores formation followed by copious washing of the residual minerals and/or sodium/potassium with deionized water from the matrix²⁴. The removal of silicon cations owing to the alkaline cations is reported elsewhere²⁵. The other reason can be thought is the concentration of OH ions which in turn regulates the pH during solvent intercalation. The concentration of OH ions in turn relates to the concentration of the intercalating agent. The effect of solution pH on the porosity is well established^{26,27}.

Effect of holding time

Baked clay was subjected to activation for time duration of 5 hr, 15 hr and 24 hr. The changes in pore properties as a function of holding time are provided in Tables 3. The surface area determined at zero time in case of NaOH was 96.00 m² g⁻¹ and in case of KOH was 96.00 m² g⁻¹. The time was then increased to 5 hr. The value obtained in case of NaOH was 111.31 m² g⁻¹, and in case of KOH was 201.28 m² g⁻¹. The time was then extended up to 15 hr. The value noted in case of NaOH was 114.74 m² g⁻¹, and in case of KOH was 131.00 m² g⁻¹. The time was further extended to 24 hr. The value obtained in case of NaOH was 140.48 m² g⁻¹, and for KOH treated sample was 129.60 m² g⁻¹.

Table 3. Changes in surface area, pore width, & micropore volume as a function of holding time.

Holding Time (hrs)	Surface area (m ² /g)		Pore width (Å)		micropore volume (cc/g)	
	NaOH	KOH	NaOH	KOH	NaOH	KOH
0.0	96.00	96.00	6.250	6.250	0.03	0.03
5.0	111.31	201.28	7.181	6.955	0.03	0.03
15	114.74	131.00	6.972	7.633	0.04	0.07
24	140.48	129.60	7.188	7.716	0.04	0.05

It is evident from the data that the time shows a positive effect on the surface area in case of NaOH while in case of KOH, the extension in time shows adverse effect.

The nitrogen adsorption isotherms of the aforementioned original and variously intercalated samples are provided in Figs. 5 (a) & 5 (b). All the isotherms obtained reveal hysteresis loop with a definite plateau. The major nitrogen adsorption occurs at low relative pressures indicating that the material is porous with narrow pore size distribution. Upon comparing the isotherms obtained in case of sodium and potassium intercalations undertaken for 0 hr, followed by 1 hr, followed by 15 hr, followed by 24 hr, it is evident that porosity of the clay under study was increased significantly when the intercalation was performed for 24 hr in case of sodium while in case of potassium, 5 hr caused significant improvement in porosity. Time extension beyond 5 hr gave a rather unimpressive effect.

Fig. 5 (a). Nitrogen adsorption-desorption isotherms of original clay and clay intercalated with NaOH as a function of holding time: 1 = Virgin and Zero time, 2 = 5hr, 3 = 15hr, 4 = 24hr.

Fig. 5 (b). Nitrogen adsorption-desorption isotherms of original clay and clay intercalated with KOH as a function of holding time: 1 = virgin and zero time, 2 = 5hr, 3 = 15hr, 4 = 24 hr.

To evaluate the influence of time on the pore width, experiments were performed with the same intercalating agents used in the mixing ratio mentioned as above. The average pore width determined at zero time in case NaOH was 6.250 Å, and in case of KOH was 6.250 Å. The value obtained in case of 5 hr intercalation with NaOH was 7.181 Å, while in case of KOH was 6.955 Å. The value determined in case of 15 hr intercalation with NaOH was 6.972 Å, and with KOH was 7.633 Å. Upon extending time up to 24 hr, the values obtained were; for NaOH, 7.188 Å and for KOH, 7.716 Å, respectively.

The influence of time was also studied on the micropore volume determined. The values determined at zero time were; in case NaOH, 0.03 cc/g, and in case of KOH, 0.03 cc/g. In case of 5 hr holding time, the values were: for NaOH, 0.04 cc/g and for KOH, 0.07 cc/g. In case of 15 hr holding time, the values obtained were; for NaOH 0.04 cc/g, for KOH, 0.05 cc/g and in case of 24 hr holding time, the values obtained were; NaOH, 0.05 cc/g and KOH, 0.05 cc/g.

There are several reasons to endorse the above mentioned findings. The holding time usually has a positive effect on porosity generation which in turn relates to the effective leaching of the other inorganic elements by the respective leachant^{28,29}. This leads to alteration in surface morphology, modification in crystal structures and interlayer spacing. The positive effect of holding time in case of sodium hydroxide is attributed due to the fact that increasing holding time ensures effective hydration, and hence imbibition of intercalating solution in to the micropores of the clay under study which in turn caused porosity generation. The effect in case of potassium hydroxide intercalation, however,

shows a reverse trend. This in turn relates to the solubility of the metal ion which is a function of molecular weight. The potassium ion is larger than the sodium ion, hence potassium ion is partially hydrolyzed in water compared to sodium at 150 °C. This poor solubility might have caused poor imbibition in to the matrix upon prolonged holding time. Another reason might be the accumulation of larger potassium ions around the pore mouths, thereby clogging the pores entrances and hence inhibiting the solvent intercalation process.

SEM study

Scanning electron microscopic study of the original clay and clay intercalated separately with NaOH & KOH at 150 °C was performed. The corresponding SEM micrographs are provided in Fig. 6. In case of original sample, the surface roughness can be seen in the form of kernels, notches, slots and kerfs which evident that the clay under study is porous. The SEM of clay intercalated with NaOH at 150 °C shows generation of pores drilled in to the matrix. The SEM of KOH intercalated sample picturing more roughness and valley shaped formations. Pores drilled in to the matrix are numerous in the form of black spots. Thus, it is established that KOH was more effectively inserted in to the clay matrix, hence generating significant porosity.

Fig. 6. SEM micrographs of original and variously intercalated clay samples (a) original (b) clay intercalated with NaOH at 150 °C (c) clay intercalated with KOH at 150 °C.

XRD study

As afore mentioned, the porosity was considerably increased in case of NaOH & KOH intercalations performed at a temperature of 150 °C compared to intercalations performed at 500 & 750 °C. To establish any changes in the composition of original clay and upon intercalations with NaOH & KOH, XRD study of selected samples was performed.

The XRD pattern of original clay is provided in Fig. 7 (a). A very intense and sharp peak can be seen at $2\theta = 12.1^\circ$ with d-spacing of 7.31 Å. The XRD pattern of NaOH intercalated sample is provided in Fig. 7 (b). It can be seen that peak appearing in the original clay sample is slightly shifted and now appearing at $2\theta = 11.9^\circ$ with d-spacing of 7.46 Å.

The data show a shift in the 2θ value from 12.1° to 11.9° with a slight increase in the d spacing value from 7.31 to 7.46 Å. This increase in the d value corresponds to increase in the interlayer spacing indicating that sodium was effectively inserted in to the clay matrix.

The XRD pattern of KOH intercalated sample is provided in Fig 7 (c). It can be seen that peak appearing in the original clay sample is now appearing at $2\theta = 13.7^\circ$ with d-spacing of 13.65 Å.

Fig. 7. XRD patterns of original and variously intercalated clay samples (a) original clay (b) clay intercalated with NaOH at 150 °C (c) clay intercalated with KOH at 150 °C.

The XRD pattern of KOH intercalated clay sample show very prominent shift in the 2θ value from 12.1° to 13.7° with pronounced increase in the d value from 7.31 to 13.65 Å. From this increase, it is inferred that KOH is more effectively inserted as compared to NaOH, thereby causing significant generation in porosity.

CONCLUSIONS

Surface area of the pre-baked clay was increased significantly when the sample was treated hydro thermally at 150°C . The increase was quite appreciable in case of potassium hydroxide compared to sodium hydroxide as intercalating agent. Increasing temperature beyond 150°C showed an adverse effect on surface properties.

The effect of mixing ratio was meaningful. An increase in surface area was noticed while increasing the mixing ratio in case of both intercalating agents.

The influence of holding time was meaningful in case of sodium hydroxide. Increase in holding time beyond 5 hr, showed deleterious effect in case of potassium hydroxide.

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